

## Effects of Different Parameters on Molybdenum Concentration in Zn-MO-Mn Alloy

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### ABSTRACT

Molybdenum is an active metal possessing high degree of corrosion resistance, hardness, high conduction along with magnetic properties. Alloy containing Zinc, Molybdenum and Manganese have been studied in this paper. The change in properties due to change in temperature, pH and current density, duration of deposition and concentration of Molybdenum in electrolytic solution were the basis of experiments conducted in this paper. The electrolytic concentration and current density produce complimentary effects to a large extent. Effect of various parameters specified above on the concentration of Molybdenum in Zn-Mn-MO alloy have been studied in this paper.

**KEYWORDS:** Molybdenum, Electrolytic deposition, Current density, Temperature

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### INTRODUCTION

The ongoing miniaturization of devices and the necessity to improve performance or enable new functions in micro-systems requires the accurate synthesis of materials with complex structures, including alloys and inter-metallic or semiconductor compounds. In extreme cases the required functionality may need nano- to atomic-scale control of the placement of atoms at predetermined locations. Electrochemical deposition has considerable potential to successfully overcome this challenge. The possibility to finely control the degree of irreversibility of the growth process via over potential, along with the ability to exploit interatomic interactions to guide growth, due to the low energy of the metal ion precursors represents only two of the multiple advantages of this technique.

The electrodeposited alloys are widely used to produce printed circuits, high speed tools, surgical instruments etc. to protect base material from corrosion meanwhile giving a pleasing, decorative appearance to the articles. The deposited alloy plates can be relatively denser and harder while having better magnetic properties than pure metals. These

alloys are used to make base metal relatively resistant to abrasion, corrosion, wear and tear. This property is effectively utilized in computers, space technology and production of decorative coatings. The probable magnetic properties enable them to be used in various electronic applications.

Molybdenum is an active metal, possessing high degree of corrosion resistance along with hardness, high conduction, high temperature and magnetic properties; thus, suitable for magnetic recording applications. Several binary and ternary alloys containing Molybdenum have been electrodeposited (1,2). Binary deposits containing Molybdenum have been found to be quite dense while displaying adherent wear and corrosion resistance (3). Ternary alloys containing Molybdenum, have gained attention in recent years owing to their remarkable resistance to tarnish and corrosion (4). A few of them were found to be magnetic and highly conductive in nature, suitable for magnetic recording. A brief survey of the relevant literature shows that many alloys containing Molybdenum which have been electrodeposited mainly from acetate bath, citrate bath, tartrate or

sulphate bath, have been found to be exceptionally corrosion resistant along with excellent smoothness and phosphating performance.(5,6,7)

## METHODS OF ELECTRODE POSITION

Electrode position is a film growth process that consists of the formation of metallic or semiconducting coatings on conductive substrates, starting from metal ion precursors in a suitable solvent and occurring via charge transfer process. (8,9,10,11)

Alloys are generally electrodeposited from aqueous solutions containing constituent metal ions. Often, it becomes necessary to use baths of complex salts to avoid rough and less adherent deposits. In recent years, electrode position of alloys has been carried out in non-aqueous solution in order to avoid electrodepositable Hydrogen. Although, deposition potential of the metals is likely to be closer together than that in aqueous solutions (12). Thus, the process of electrode position in aqueous medium has been widely accepted owing to the nontoxic, less expansive, nature of the medium. The components of electrolytic bath have individual roles to play in the deposition of metals, whereas the substrate material usually controls its kinetics. There are some important parameters which influence the deposition process due to pH of the solution, temperature of the bath, current density, duration of deposition, agitation, presence of addition agents etc.

The mechanism of ternary alloy deposition is more complex than single metal deposition (13). Electrode position of metal is a process in which metal ion after getting rid of its sheath of solvent molecules or complex anions, combines with the equivalent number of electrons to become a neutral atom and gets incorporated into the crystal lattice of the cathodically formed deposit. The code position of two or more metals has been explained mainly on the

basis of thermodynamic data particularly on the kinetic reduction of various alloy components in the pure form.

Electrolysis of the solution was carried out in an electrolytic cell (14,15). The electrolytic cell and electrodes were thoroughly cleaned. Then, the cell was filled with 225ml of fresh electrolytic solution and placed in a water thermostat to aid temperature control. After inserting the electrodes in position, the electrolysis was carried out for 30 minutes, under different plating conditions at current density of 2.0-6.0  $\text{ADM}^{-2}$ . A D.C. stabilized power supply provided current for this process to ensure a constant flow of current during deposition.

Electrodeposited alloys are generally considered to be crystalline in structure. The external appearance and physical properties mainly depend on the rate of crystal growth and formation of nuclei. The deposit may be smooth, fine grained and adherent if the plating conditions are such as to favor the rapid formation of crystal nuclei.

## DETERMINATION OF ALLOY COMPOSITION

The film deposited at the cathode were washed with distilled water, dried, and then scratched carefully. A fixed amount 50 mg of the alloy was dissolved in 50 ml of distilled water containing 2-3 drops of sulphuric acid for analysing its various metal constituents. Manganese and Molybdenum were estimated by usual colorimetric methods while the amount of Zinc was determined titrimetrically using diphenyl benzidine as an indicator. The influence of different plating variables such as temperature, current density, duration of deposition, pH and metal concentration in the bath on the deposition of Molybdenum has been studied. Semi bright, light grey, smooth and adherent deposits are generally formed.

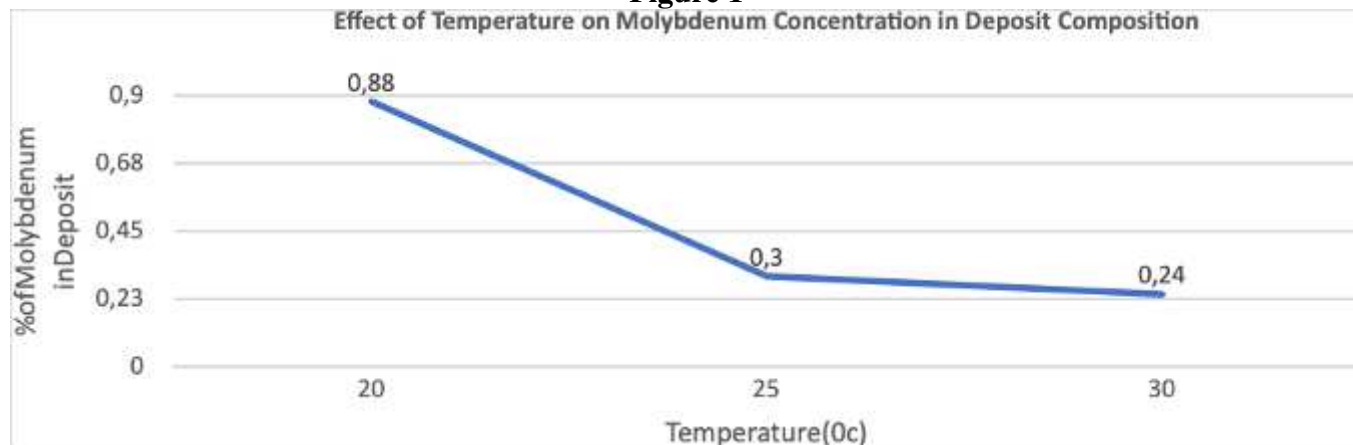
## RESULT AND DISCUSSION

### Effect of Temperature on Molybdenum Concentration in Deposit Composition

Experiment was conducted to study the influence of variation of temperature on alloy deposition i.e., Molybdenum in citrate bath. Results are consolidated in table 1 along with its effects in fig. 1. It was observed that Molybdenum content in the deposits decreased with the increase in temperature. At temperature greater than 30 °C, no deposition has been observed.

Table 1

S. no.	pH	Temperature (°C)	Molybdenum in solution ( $\text{gL}^{-1}$ )	Current Density ( $\text{ADM}^{-2}$ )	Time of deposition (min)	Molybdenum in deposit (%)
1	2.05	20	4.0	4.0	30 min	0.88
2	2.05	25	4.0	4.0	30 min	0.30
3	2.05	30	4.0	4.0	30 min	0.24
4	2.05	35	4.0	4.0	30 min	0.00

**Figure 1**

Bath compositions ( $\text{gL}^{-1}$ ): Zinc sulphate 30.0, Manganese sulphate 60.0 Ammonium molybdate 4.0, citric acid 5.0 starch 1.0

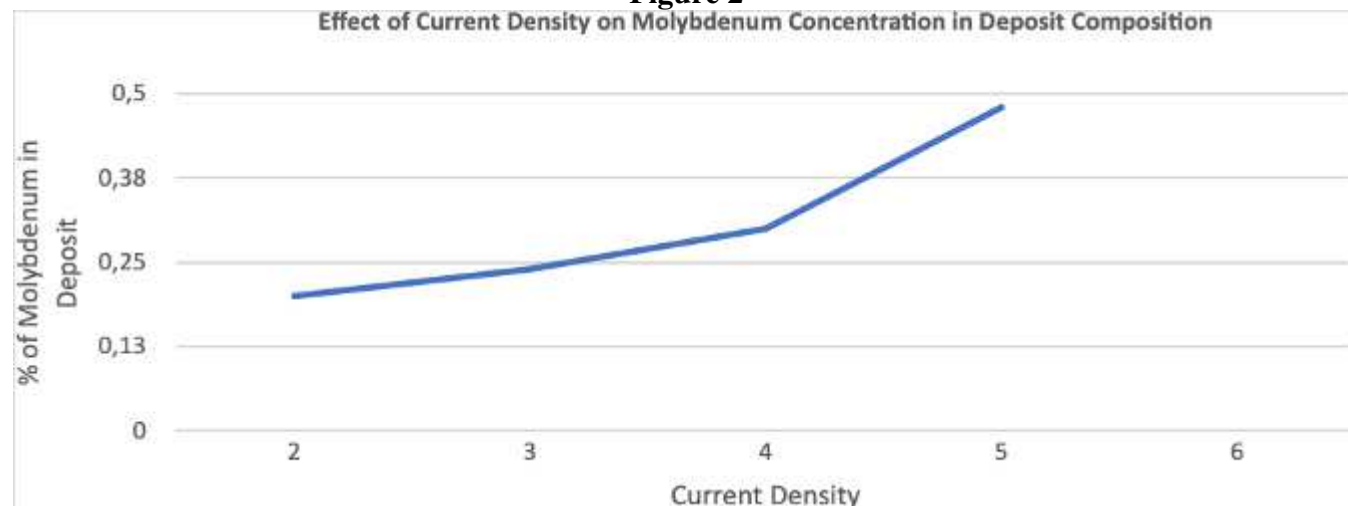
### Effect of Current Density on Molybdenum Concentration in Deposit Composition

Current density is one of the salient parameters that influence the deposit composition. Results are shown in table 2 and fig.2. On increasing the current density, percentage of Molybdenum in deposit also increases although deposit obtained is dark grey, uneven, crystalline in nature and the grains are larger in size with a scattered gathering. At lower current densities, the discharge of ions occurs slowly, as a result of which: rate of growth of nuclei becomes higher than the rate of formation of fresh nuclei leading to coarsely crystalline deposits. As current density is raised, the rate of formation of fresh nuclei increases making the deposit finer grained. At very high current densities, the metal ions near the cathode gets removed quickly leading to brittle or no deposition as the region becomes short of the ions required for discharge. Hence, the crystals tend to grow outwards- towards regions of higher metal concentration, giving deposits consisting of trees and nodules.

Generally, the properties of less noble metals in the deposited alloy should also increase with increasing current density. The effect is more marked when co-depositing metals are in complex ions with common anions than when the anions of complex ions are different.

**Table 2**

S. no	pH	Temperature (°C)	Molybdenum in solution ( $\text{gL}^{-1}$ )	Current Density ( $\text{ADM}^{-2}$ )	Time of deposition (min)	Molybdenum in deposit (%)
1	2.05	25	4.0	2.0	30 min	0.20
2	2.05	25	4.0	3.0	30 min	0.24
3	2.05	25	4.0	4.0	30 min	0.30
4	2.05	25	4.0	5.0	30 min	0.48
5	2.05	25	4.0	6.0	30 min	0.60

**Figure 2**

Bath compositions ( $\text{gL}^{-1}$ ): Zinc sulphate 30.0, Manganese sulphate 60.0 Ammonium molybdate 4.0, citric acid 5.0 starch 1.0

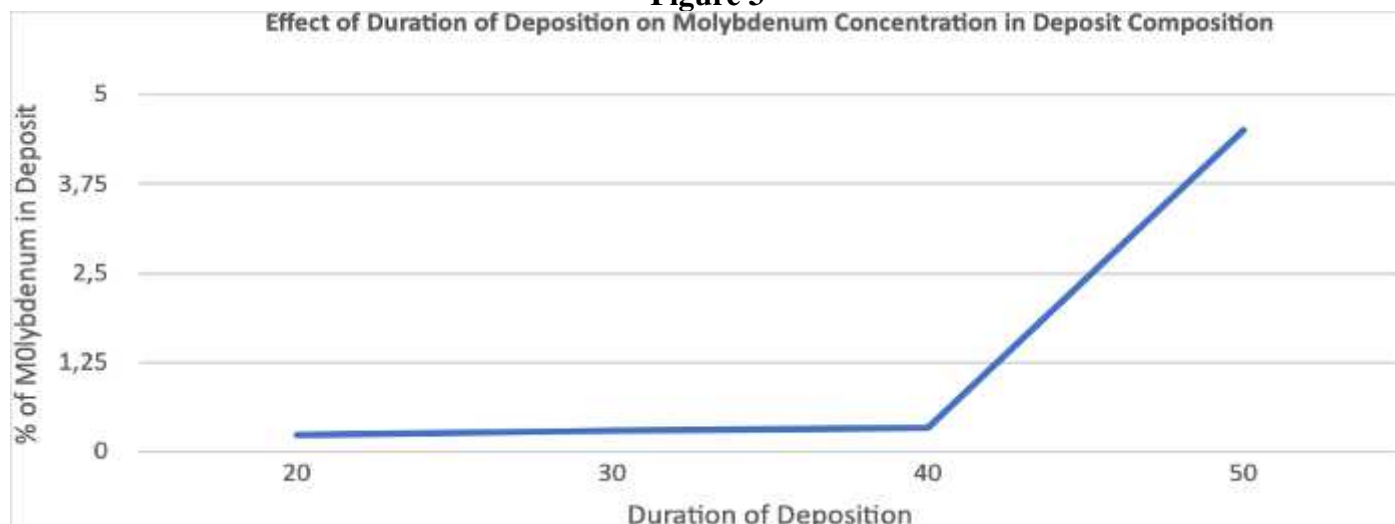
### Effect of Duration of Deposition on Molybdenum Concentration in Deposit Composition

The study of influence of duration of deposition on molybdenum concentration in deposit composition at 25 °C, a pH of 2.05, and current density of 4.0 ADM<sup>-2</sup> for a duration of 20 min, 30 min, 40 min, 50 minutes was carried out from the current bath and the results are stated in table 3 and fig. 3. The alloy is deposited in the composition range from 96.46 – 99.78 % zinc, 0.06 -3.18% manganese and 0.16-0.78% molybdenum with the time of deposition. It is evident from table that the percentage of molybdenum in the deposit increases with increasing time of deposition. This might be due to the gradual utilization of more current by molybdenum as the time of deposition increases.

**Table 3**

S. no	pH	Temperature (°C)	Molybdenum in solution (gL <sup>-1</sup> )	Current Density (ADM <sup>-2</sup> )	Time of deposition (min)	Molybdenum in deposit (%)
1	2.05	25	4.0	4.0	20 min	0.24
2	2.05	25	4.0	4.0	30 min	0.30
3	2.05	25	4.0	4.0	40 min	0.34
4	2.05	25	4.0	4.0	50 min	0.42

**Figure 3**



Bath compositions (gL<sup>-1</sup>): Zinc sulphate 30.0, Manganese sulphate 60.0 Ammonium molybdate 4.0, citric acid 5.0 starch 1.0

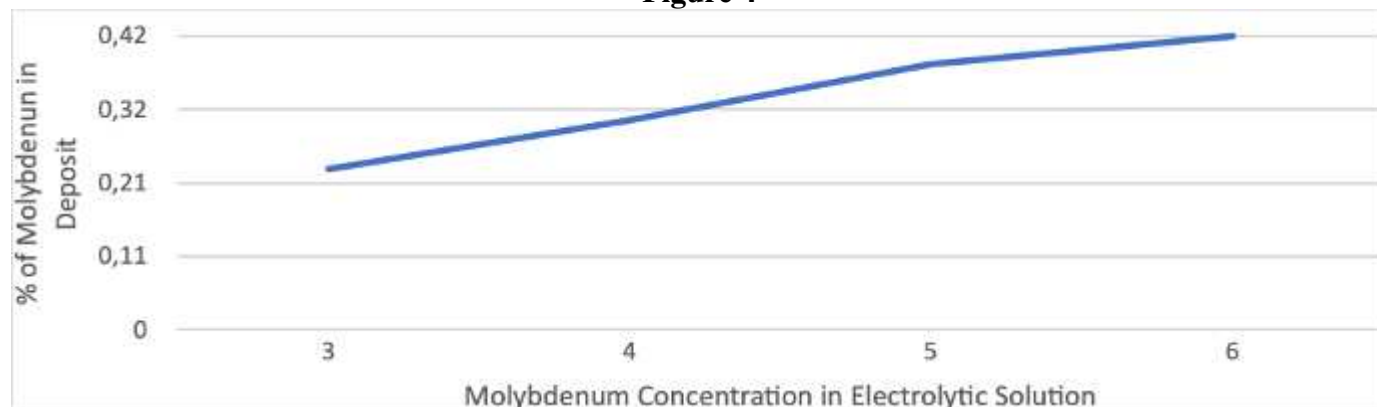
### Effect of Molybdenum Concentration in Electrolytic Solution on Molybdenum Concentration in Deposit Composition

Table 4 and fig. 4 demonstrates the effect of varying concentration of the constituent metal ion in the bath on deposit composition. When the molybdenum concentration in the plating solution is increased, its concentration in the alloy gradually increases. An increase in the concentration of a particular metal ion in the plating solution might facilitate the nucleation of that ion in the deposit, resulting in an increased concentration, evident from the examination of the distribution of total current utilised by different ions for their deposition.

**Table 4**

S. no	PH	Temperature (°C)	Molybdenum in solution (gL <sup>-1</sup> )	Current Density (ADM <sup>-2</sup> )	Time of deposition (min)	Molybdenum in deposit (%)
1	2.05	25	3.0	4.0	20 min	0.23
2	2.05	25	4.0	4.0	30 min	0.30
3	2.05	25	5.0	4.0	40 min	0.38
4	2.05	25	6.0	4.0	50 min	0.42



**Figure 4**

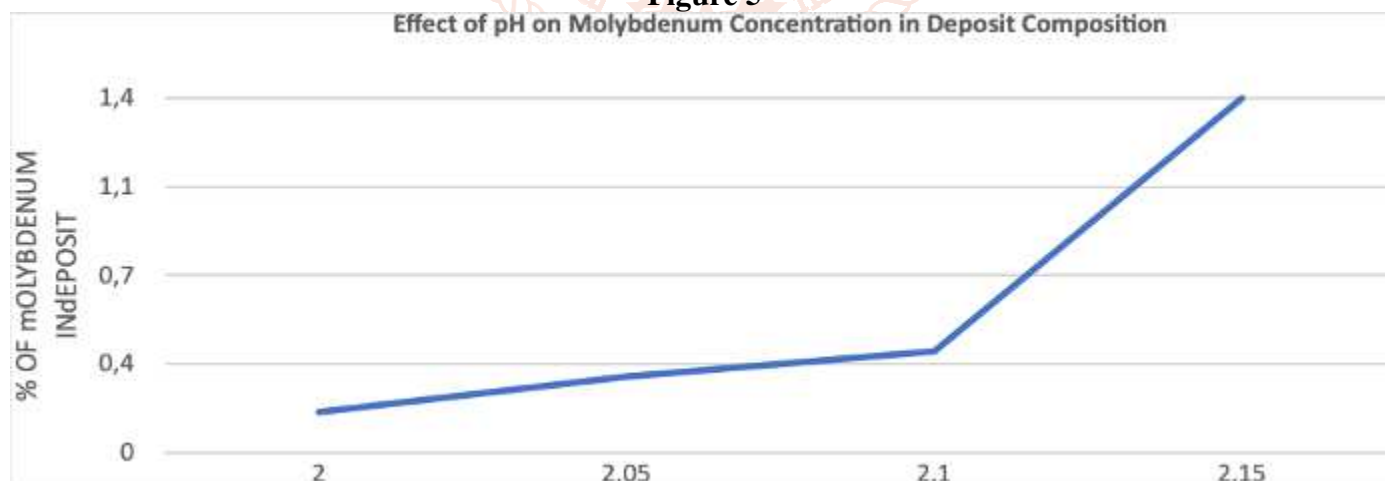
Bath compositions ( $\text{g/L}^{-1}$ ): Zinc sulphate 30.0, Manganese sulphate 60.0 Ammonium molybdate 4.0, citric acid 5.0 starch

### Effect of pH on Molybdenum Concentration in Deposit Composition

The effect of variation in pH values at different current densities on alloy composition and cathode current efficiency for the deposition of molybdenum at  $25^\circ\text{C}$  is given in table 5 and fig. 5. It is clear from the table that the percentage of molybdenum in deposits increase with the increasing current density and pH of the solution. Since the metal of relatively higher position in the oxidation-reduction potential series are chemically more active than those at a lower position, it will plate out of the solution with difficulty. Meanwhile, if hydrogen ions are present in the electrolyte bath, ions of a metal lower than hydrogen in the e.m.f. series would get deposited rather easily than the ions of those metals lying above hydrogen. Hence, with increasing pH of the solution the deposition of molybdenum will be facilitated but morphological feature of alloy become dissatisfactory. Blackish-grey, uneven, crystalline deposit are formed at higher pH values.

**Table 5**

S. no	pH	Temperature ( $^\circ\text{C}$ )	Molybdenum in solution ( $\text{g/L}^{-1}$ )	Current Density ( $\text{ADM}^{-2}$ )	Time of deposition (min)	Molybdenum in deposit (%)
1	2.00	25	4.0	4.0	30 min	0.16
2	2.05	25	4.0	4.0	30 min	0.30
3	2.10	25	4.0	4.0	30 min	0.40
4	2.15	25	4.0	4.0	30 min	1.40

**Figure 5**

Bath compositions ( $\text{g/L}^{-1}$ ) Zinc sulphate 30.0, Manganese sulphate 60.0 Ammonium molybdate 4.0, citric acid 5.0 starch 1.0

### MORPHOLOGY

The morphological results of the alloy plates obtained under various conditions of electrode position are summarized in table mentioned below. The photomicrographs of electroplates indicate that grey, even, fine grained, compact deposits are favored by decreasing the pH value and current density whereas on the other hand, they become uneven, blackish grey crystalline deposit at lower temperatures. Their brightness increases when the concentration of molybdenum in the bath increases or time of deposition decreases.

**MORPHOLOGICAL RESULTS**

S. no.	pH	Current density (ADM <sup>-2</sup> )	Time of deposition (Min)	temperature (°C)	Molybdenum concentration in solution (gL <sup>-1</sup> )	Morphology
1	2.05	4.0	30	25	4.0	Smooth, light grey, compact, large grain sized grains
2	2.05	6.0	30	25	4.0	Dark grey, uneven, crystalline deposit with a scattered gathering of grains of the larger size
3	2.0	4.0	30	25	4.0	Smooth, light grey, compact deposit
4	2.15	4.0	30	25	4.0	Blackish grey, uneven, crystalline deposit
5	2.05	4.0	30	20	4.0	Blackish grey deposit with large grains
6	2.05	4.0	30	35	4.0	No deposition
7	2.05	4.0	30	25	5.0	Even, fine grained uniform grey deposit
8	2.05	4.0	20	25	4.0	Even, fine grain compact deposit with a few scatterings gathering of grains of large size
9	2.05	4.0	40	25	4.0	Dark grey, uneven crystalline deposit compact with scattered gathering of grains of large size

**CONCLUSION**

In this work, the influence of various parameters on electrode position of molybdenum in Zn-Mn-Mo in citrate baths was studied. It was observed that percentage of molybdenum increased in the deposits facilitated by an increase in current density and pH of the solution although, the morphological feature of alloy became worst. Blackish grey, uneven, crystalline deposit with a scattered gathering of grains of the larger size were obtained. When the molybdenum concentration in the plating solution was increased, its concentration in the alloy also gradually increased with grey, even, fine grained, compact deposits. It was also found that the percentage of molybdenum in the deposit increases with increasing the time of deposition. Also, it has been observed that Molybdenum content in the deposits decreased with an increase in temperature. At temperature greater than 30°C and a pH of 2.05, no deposition was observed.

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